A Soft and Efficient Approach for Removal of Template from Mesoporous Silica using Benzene Sulfonamide

Mohammad Teymouri [1*], Abdolraouf Samadi-Maybodi [2], Amir Vahid [1,2]

[1] Research institute of petroleum industry, Tehran, Iran
[2] Analytical division, Faculty of Chemistry, University of Mazandaran, Babolsar, Iran

Abstract

In this contribution, an effective and soft method for removal of template from nanochannels of mesoporous silica (MCM-41) is proposed. This method is based on chemically-modified solvent extraction which enhanced by means of an auxiliary organic compound, i.e. benzene sulfonamide. Template removal was performed in soft condition, i.e. in the presence of diluted sulfuric acid and at ambient temperature. Presence of benzene sulfonamide extremely improves efficiency of template removal process. The template-extracted mesoporous silica was characterized using powder X-ray diffraction, nitrogen adsorption, transmission electron microscopy, thermogravimetry, elemental analysis and FT-IR spectrometry. Results of XRD, nitrogen adsorption, and TEM displayed that well-ordered hexagonal array of mesopores remained intact after extraction. The obtained results from thermogravimetry, elemental analysis and FT-IR spectrometry indicate that at least up to 94 wt % of template was removed in short time.

*Keywords***:** Template removal; Mesoporous silicate material; Extraction; Benzene sulfonamide; Highly ordered

1. Introduction

MCM-41 is an organic-inorganic composite that formed from close packed silica-coated micelles of a surfactant template [1]. Composite precursor to MCM-41 can contain as much as 55% organic material by weight. Elimination of the template via a proper method leaves mesoporous parallel channels in a honeycomb array [2-4]. Generally, the surface and pore properties of mesoporous materials like number of hydroxyl groups, relative hydrophobicity and size of unit cell are of vital importance for diverse applications such as adsorption [5], catalysis [6], separation [7], drug delivery [8], medicine [9], photonic [10] and as support for embedding of biomolecules [11,12] and nanoparticles [13]. The removal of template is an important step in the preparation of MCM-41 because different removal methods certainly influence the surface and pore properties of MCM-41 [3, 4].

The most common method to remove the template is calcination owing to complete elimination of template and higher hydrothermal stability of final product due to the higher cross-linking degrees of mesoporous

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* Corresponding Author: E-mail address: teymourim@ripi.ir

materials [14]. The main drawbacks of calcination are the unrecovery of surfactants, the sacrifice of other organic functional groups [15], extensive silanol condensation marked shrinkage of the mesostructure [16], very slow heating rates as low as 1 °C/min to 550 °C which followed by an extended period of heating at that temperature [17], expensive muffle furnace and production of terrible smells and toxic gases [18-20]. Microwave digestion was also applied for the removal of template from mesoporous materials. A mixture of concentrated HNO_3 and H_2O_2 at high temperature and pressure can assists oxidation of the surfactant molecules and completely remove them within minutes, result in highly ordered inorganic frameworks with rich silanol groups [21]. Microwave-sensitive materials such as activated carbon can generate instantaneous high temperature when irradiate at moderate heating power, which facilitate the entire elimination of template [17]. Ultraviolet irradiation simultaneously can generate strong oxidants ozone and oxygen atom and break C-C bonds in organic surfactants and hence decompose them. Therefore, photochemical decomposition of organic molecules under irradiation with a high energy vacuum ultraviolet light can perform at room temperature to the preparation of mesoporous silica films. Photocalcination technique is applicable to the elimination of any organic molecules from a wide variety of mesostructures fabricated using templates of organized molecular assemblies [22]. Supercritical fluid extraction was employed to extract and recover organic template from mesoporous silicate materials. Supercritical fluids such as CS_2 and CO_2 have better solubility than normal solvents and therefore are more efficient [23, 24].

Solvent extraction is a mild and conventional method to remove surfactants and get porosities without distinct effects on framework [25]. Ethanol with small amount of hydrochloric acid can be used as an organic solvent [26, 27]. In some cases extraction was combined with temperature-controlled calcination at low temperature (200 to 400 °C). This method was shown to be effective for the template removal from the cage-like materials like SBA-16 [16]. Extraction can get silicate materials with larger pore size in some cases. Much more surface hydroxyl groups can also be kept; enhancing the hydrophilic property of mesopores and providing a possibility for a high degree of post-functionalization of the pore wall surface. On the other hand, the application of extraction is limited by its low efficiency which prevents to achieve high pore volume and large pore size [10].

However, the most important requirements i.e. ideal structural properties of inorganic framework, high efficiency removal of template, low operation time, simple instrumentation and easy procedure cannot be simultaneously achieved by any of the above-mentioned methods.

In the present work, removal of template from nanochannels of MCM-41 was performed using a highly efficient, rapid, mild and simple method. The extracted MCM-41 was characterized by powder X-ray diffraction, nitrogen physisorption, thermogravimetry and elemental analysis.

2. Experimental

2.1. Materials and synthesis of MCM-41

Cetylmethylammonium bromide (CTAB), tetraethylorthosilicate (TEOS), aqueous ammonia (25% w/w), ethanol (99.5%) and sodium acetate trihydrate all were purchased from Merck and were used without purification. In a typical synthesis of MCM-41, CTAB was dissolved in a mixture of water/ethanol and then the ammonia solution and sodium acetate were added to this solution. After about 10 min stirring at 200 rpm a clear solution was obtained. Then the TEOS was added to this solution. The final molar composition of the resulting gel was TEOS: 1; CTAB: 0.22; Sodium acetate: 0.34; NH_3: 11; Ethanol: 1; Water: 155. After 2.5 hours stirring at room temperature, the obtained gel was transformed to a Teflon-lined stainless-steel vessel and aged at 70 °C for 12 hours. Finally the white precipitate was filtered and washed with appropriate amount of water and then dried at 100 °C in oven over night. The as-synthesized sample was calcined in air at heating rate of 1 °C/min up to 500 °C and held at this temperature for 5 hours.

2.2. Template removal by extraction

Step 1. An aqueous solution (containing 8 % v/v of ethanol) of Sulfuric acid with concentration of 1.8 mol/l was prepared. Then 50 milliliters of this solution was mixed with 2 grams of as-synthesized MCM-41 and 0.25 gram of benzene sulfonamide. This mixture was stirred at 1200 rpm with a 1 cm magnet bar. Steering was continued for 15 minutes and the suspension was filtered and washed with 50 milliliters of deionized water. This procedure was repeated five times.

*Step 2. T*he acid-treated MCM-41 (obtained at the end of step 1) was added to the 50 milliliters of 1.8 mol/l ethanolic solution of sulfuric acid. This suspension was stirred at 1200 rpm for 5 minutes. Then the mixture was filtered and washed with 50 milliliters of ethanol. This procedure was repeated twice. All steps were performed at ca. 35 °C. Finally, the template-extracted (acid treated) MCM-41 dried at 100 °C in oven over night.

2.3. Characterization

Transmission FT-IR spectra were recorded using a Bruker VERTEX 22 spectrometer. X-ray diffraction (XRD) patterns were recorded by a GBC MMA diffractometer with beryllium Filtered Cu K α radiation (1.5418 Å) operating at 35.4 kV and 28 mA. Diffraction data was recorded between 1 and 9° 2θ with a resolution of 0.01° 2θ with the scan rate of 1.0 2θ/min. Scanning electron micrographs were recorded using a Zeiss DSM 962 (Zeiss, Oberkochen, Germany). The sample was deposited on a sample holder with an adhesive carbon foil and sputtered with gold. Adsorption/desorption of nitrogen was carried out at -196 °C using a BELSORP-mini sorptometer. Prior to analysis the samples were outgassed in-vacuo for 6 hours at 100 °C until a stable vacuum of 0.1 Pa was reached. Pore diameter was calculated by geometrical (pressure independent) method [28-30]. Thermogravimetric experiments were performed on Rheometric simultaneous thermal analyzer (STA 1500). Weight change curves were recorded in flowing air with a heating rate of 5 °C/min from room temperature up to 800 °C. Elemental analysis was performed using PerkinElmer 2400 (Series II) CHNS elemental analyzer for determination of carbon, hydrogen, nitrogen and sulfur residue of parent, extracted and calcined MCM-41 material. Transmission electron microscopy was performed by Carl Zeiss Leo 912 AB with a tension voltage of 120 kV. Samples were dispersed in ethanol and sonicated for 15 minutes and deposited on a copper grid.

3. Results and discussion

Presence of an auxiliary organic compound, i.e. benzene sulfonamide, is a key factor in this template removal approach. We suggest that hydrophobic part of benzene sulfonamide, i.e. benzene group improve penetration of molecule through the close packed silica-coated micelles of CTAB surfactant. Then, the amide group of benzene sulfonamide, which becomes cationic in acidic media, can exchange with the cationic head of surfactant molecule inside the mesopores of MCM-41. In this way, benzene sulfonamide can acts as an auxiliary compound, beside sulfuric acid and ethanol, to remarkably improve the efficiency of template removal. The MCM-41, which was obtained at the end of step 1, yet had high quantity of sulfur. The sulfur content, which was determined by elemental analysis, was about 6.8% by weight. The amount of sulfur in the as-synthesized MCM-41 which treated in the same way, but in the absence of benzene sulfonamide, was about 0.2 % which is due to the presence of residual H_2SO_4 on the surface MCM -41. As can be deduced from FT-IR spectra (figure 1), it may be due to the adsorption of benzene sulfonamide on MCM-41. Figure 1 shows the FT-IR transmission spectra of *a*: as-synthesized, *b*: extracted MCM -41 at the end of step 1 after proper washing and drying, *c*: extracted MCM -41 at the end of step 2 after proper washing and drying and *d*: calcined MCM -41 (calcined in air at heating rate of 1 °Cmin^{-1} up to 500 °C and held at this temperature for 5 hours), respectively.

A broad band around 3440 cm^{-1} appears for all samples, which is partially caused by the O–H stretching vibration mode of the adsorbed water molecules, whose deformation vibration mode is responsible for the band recorded at 1630 cm^{-1}. The absorption bands at 1040 and 801 cm^{-1} are due to Si–O–Si and Si–O stretching vibrations, respectively. The band at 954 cm^{-1} is assigned to Si–OH stretching. Several absorption bands at around 2850–3000 and 1480 cm^{-1} shown in figure 1*a* can be assigned to C–H stretching and bending vibrations of the CTAB template. Figure 1*b* proves the existence of benzene sulfonamide in mesopores of MCM-41. Two peaks around 3350-3450 cm^{-1}, which overlapped with O–H stretching vibration band, can be assigned to N-H stretching vibrations of benzene sulfonamide. Two absorption bands at around 1340 and 1450 cm^{-1} caused by the O=S=O stretching vibrations of benzene sulfonamide.
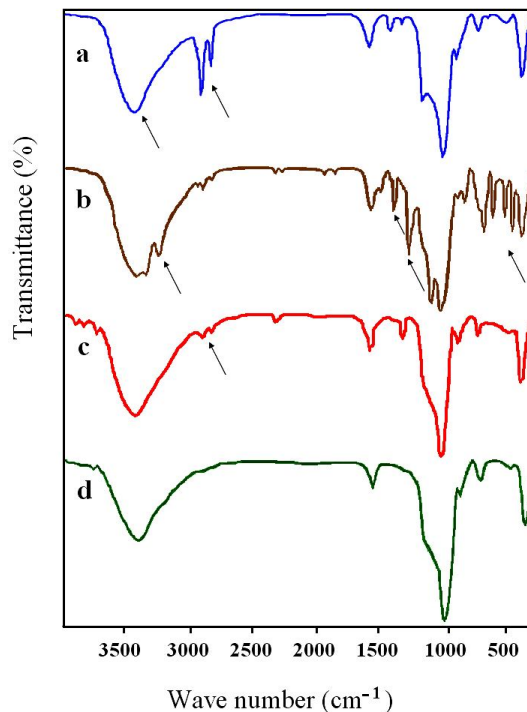
Figure. 1. FT-IR spectra of *a*: as-synthesized (M_{as}), *b*: extracted at the end of step 1, *c*: extracted at the end of step 2 (M_{ex}) and *d*: calcined (M_{cal}) MCM-41.

These peaks become indiscernible in figure 1*c*. This means that the exchanged benzene sulfonamide (during step 1) was removed from mesopores of MCM-41 at the end of step 2. As can be seen in figure 1*d*, all absorption peaks of C–H (template) completely vanished.

In order to investigate the mesoporous specific structure of samples, as well as structural properties in terms of long-range order of mesopores, PXRD experiment was performed. The PXRD pattern of as-synthesized MCM-41 (denoted as M_{as}), extracted MCM-41 or acid treated MCM-41 at the end of step 2 (denoted as M_{ex}) and Calcined MCM-41 (denoted as M_{cal}) are shown in figure 2*a*, *b* and *c*, respectively.

A prominent peak corresponding to the d_{100} plane suggests the existence of hexagonal array of pores in all samples and also is used for calculating unit cell parameter (table 1).

As can be seen, the intensity of d_{100} diffraction in the M_{ex} (figure 2*b*) shows no considerable decrease in comparison with M_{as} (figure 2*a*). This means that the extraction process does not lead to collapse of the hexagonal structure of M_{as}. This statement is supported by the presence of three higher order diffraction peaks in the PXRD pattern of M_{ex} as well as M_{as} and M_{cal}. These three diffraction peaks can be indexed to (110), (200) and (210), suggesting the presence of highly ordered hexagonal structure. After extraction, the peaks shifted slightly to higher 2θ values due to pore size contraction. As expected, the value of this shift is higher for calcined MCM-41.

**Table 1.** Physical properties of as-synthesized (M_{as}), extracted (M_{ex}) and calcined (M_{cal}) samples

Sample	S_{BET} (m^2/g)[a]	V_t (cm^3/g)[b]	a[c] (nm)	W_d(nm)[d]	W_t (nm)[e]
M_{as}	-	-	4.88	-	-
M_{ex}	939	0.69	4.76	3.85	1.09
M_{cal}	918	0.67	4.47	3.55	1.10

[a] BET specific surface area, [b] total pore volume, [c] Unit cell parameter obtained from PXRD diffractograms ($2d_{100}/\sqrt{3}$), [d] pore diameter (nm) calculated by geometrical (pressure independent) method, [e] Wall thickness (nm) obtained by following equation: $W_t = a - (W_d/1.05)$.

Teymouri et al./ Journal of Nanoanalysis No. 03, Issue 01 (2016) 26-33
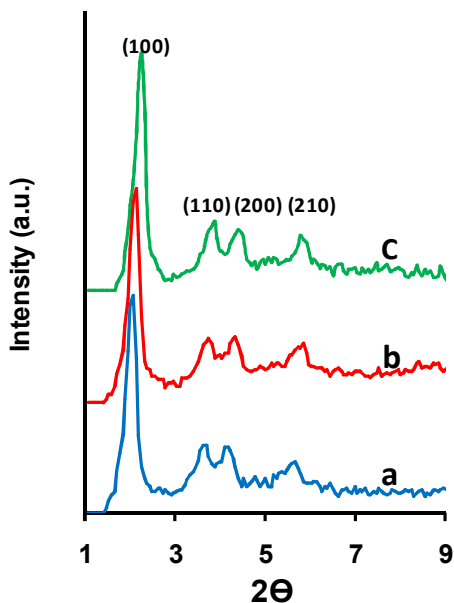
Figure 2. PXRD patterns of a: as-synthesized (M_{as}), b: extracted (M_{ex}) and c: calcined (M_{cal}) MCM-41. The PXRD patterns for b and c are offset vertically by 400(a.u.).

Adsorption/desorption of nitrogen was performed to probe and compare the textural properties of M_{cal} and M_{ex}. The isotherms of M_{cal} and M_{ex} are shown in figure 3*a* and *b*, respectively. Both isotherms can be classified as type IV according to IUPAC nomenclature, indicating that the samples retain their hexagonal mesophases after template removal either via calcination or extraction. In figure 3*b*, a linear increase in nitrogen adsorption occurs at low relative pressures (0.05-0.22) due to monolayer adsorption of nitrogen on the surface of M_{ex}. From this linear region the specific surface area was determined using BET (Brunauer-Emmett-Teller) equation. The calculated value is comparable with that found for M_{cal} (table 1).
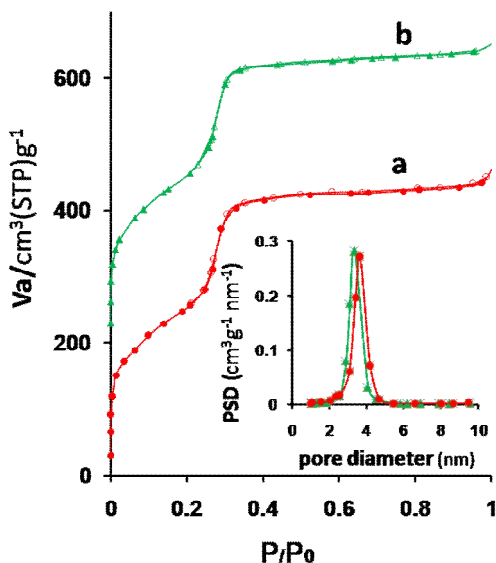
Figure 3. Nitrogen sorption isotherms of *a:* extracted MCM-41 (red curve) and *b*: calcined MCM-41 (green curve) corresponding to samples M_{ex} and M_{cal}, respectively. The isotherm for *b* (M_{cal}) is offset vertically by 200 cm^3(STP) g^{-1}. The inset is the corresponding pore size distributions (PSD) of both samples.
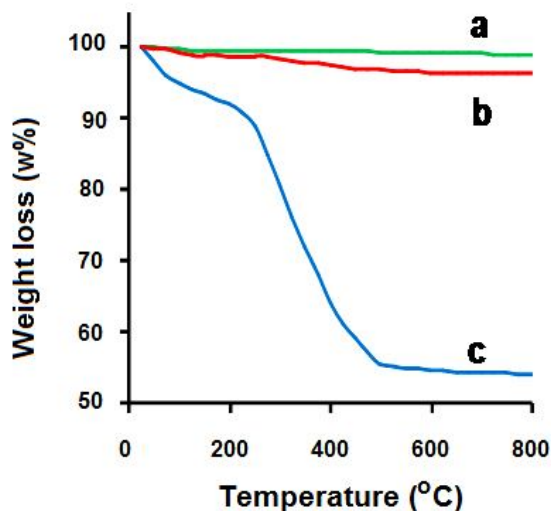
Figure 4. Thermogram for *a*: as-synthesized (M_{as}), *b*: extracted (M_{ex}) and *c*: calcined (M_{cal}) samples.

A sharp inflection over a narrow relative pressure range, at which the nitrogen uptake suddenly occurs, suggests that capillary condensation of gas take place within the mesopores and the sharpness of this region specifies that the M_{ex} has also uniform mesopores which implies that extraction process does not has significant effect on the structural order of M_{as}. Furthermore, the adsorption and desorption isotherms are almost reversible in this region. This fact specifies that the most pores within the M_{ex} are open pores, connected directly to the surface of the calcined sample and are accessible for the nitrogen molecules. These features can also be seen for figure 3*b* (M_{cal}). Nitrogen sorption isotherm of M_{cal} shows a steep rise in adsorption of gas at slightly lower relative pressure (P/P0) compared with the M_{ex}, suggesting that the former has slightly smaller pore diameter. This feature is due to the framework condensation of MCM-41 during calcination. Figure 3(inset) shows pore size distribution of M_{cal} and M_{ex}. As can be seen, both of them have narrow pore size distributions. These results are in agreement with those found in PXRD analysis. Textural properties of all samples were given in Table 1.

Thermogravimetric analysis was performed on M_{as}, M_{ex} and M_{cal} for evaluation of remaining surfactant in the mesopores of MCM-41 after extraction.

Figure 4*a*, *b* and *c* exhibits thermogram of M_{as}, M_{ex} and M_{cal} , it can be said that weight loss between 25 and 800 °C related to the surfactant decomposition, which is about 47.8, 3.1 and 1.1% for the M_{as}, M_{ex} and M_{cal} respectively. According to the obtained results, the yield of template removal (difference between the weight loss of M_{as} and M_{ex} divided by weight loss of M_{as}) was calculated as 94% which is comparable with the previous reported methods [14-27].

Elemental analysis provides further direct evidence for the amount of template in MCM-41 body. Results indicate that the extracted sample (M_{ex}) retained about 1.8% of the carbon residue, which after calcinations (M_{cal}) at 500 °C was reduced to 0.12%. The amount of carbon in M_{as} was 28.6% by weight. The template removal efficiency can also be calculated using elemental analysis results (difference between carbon residue of M_{as} and M_{ex} devided by carbon residue M_{as}). The obtained result for template removal efficiency is nearly equal to that found from thermogravimetric analysis. Additionally, the obtained results from elemental analysis was proved that the yield of applied method for template removal was about 34% higher than the method performed in the same way, but in the absence of benzene sulfonamide. This large difference is an indication of significant effect of benzene sulfonamide on the template removal yield. TEM images provide details, in real space, of the open framework structure of MCM-41 material. Figures 5a & b illustrate TEM images of M_{cal} and M_{ex}, respectively.
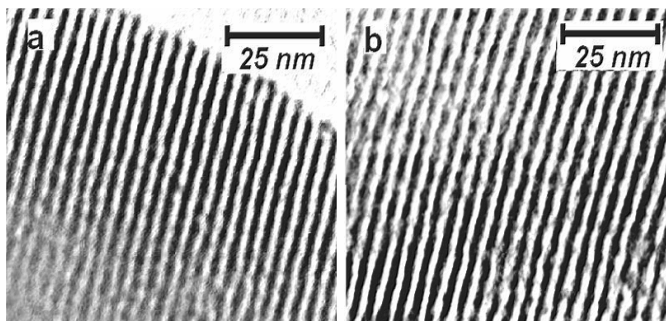
Figure 5. TEM images of a: M_{cal} and b: M_{ex} from top view, respectively.
As can be seen, both samples have well-ordered arrays of mesopores. This result further suggests that extraction of template via the above-mentioned method did not have any major effect on the degree of structural ordering of mesopores.

4. Conclusions

In this work, an efficient and to some extent method was used for removal of template from MCM-41 material using benzene sulfonamide as an auxiliary compound that improves the extraction process. Template removal was carried out at mild condition, i.e. low acid concentration and ambient temperature. The mild condition exhibits minor effects on the structural order of MCM-41. The yield of procedure was high, up to 94% by weight without considerable shrinkage on the framework of as-synthesized MCM-41 material. Other projects on the template removal from other mesoporous materials with different pore size and geometry like SBA-15, SAB-16, HMS, PMOs and other metal oxide mesoporous materials via the above-mentioned approach are in current in our laboratory.

Acknowledgements

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